END
DATE
FILMED

4 -82

DTIC

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU

AFWAL-TR-81-4141

INVESTIGATION OF CNTD SiC ON COMPLEX SHAPES

Robert A. Holzl
Jacob J. Stiglich
Rodney M. Panos

San Fernando Laboratories
10258 Norris Avenue
Pacoima, California 91331

November 1981

Final Technical Report for Period 1 July 1978 - 1 June 1981

Approved for public release; distribution unlimited.

DTIC
ELECTE
MAR 2 3 1982
B

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

82   049

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

KHODABAKHSH S. MAZDIYASNI
Project Engineer
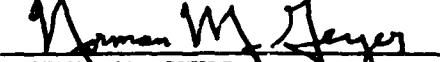
NORMAN M. GEYER
Technical Area Manager
Processing & High Temperature
  Materials Branch
Metals & Ceramics Division

FOR THE COMMANDER

HENRY C. GRAHAM, Chief
Processing & High Temperature
  Materials Branch
Metals & Ceramics Division

AIR FORCE/56780/5 February 1982 — 100

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-81-4141	2. GOVT ACCESSION NO. AD A112416	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Investigation of CNTD SiC on Complex Shapes		5. TYPE OF REPORT & PERIOD COVERED 1 July 78 - 1 June 81 Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert A. Holzl, Jacob J. Stiglich Rodney M. Panos*		8. CONTRACT OR GRANT NUMBER(s) F33615-78-C-5161
9. PERFORMING ORGANIZATION NAME AND ADDRESS 9M294 San Fernando Laboratories 10258 Norris Avenue Pacoima, CA 91331		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS FY1457-80-01050
11. CONTROLLING OFFICE NAME AND ADDRESS DCASMA Van Nuys 6230 Van Nuys Blvd. Van Nuys, CA 91408		12. REPORT DATE November 1981
		13. NUMBER OF PAGES 49
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approval for public release;
distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

*R.M. Panos is now at Litton Industries, Woodland Hills, CA.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The present report describes efforts to develop chemical vapor deposition (CVD) techniques for applying uniform coatings of structural ceramic materials to a complex shape. Both Si_3N_4 and SiC were used in the program, and the shape chosen to demonstrate the capabilities of the specially designed reactor was an airfoil--in particular a Si_3N_4 vane

(over)

DD FORM 1473   EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73

and a SiC blade.

The complete program encompassed two major efforts the first of which resulted in a chamber in which CVD Si_3N_4 was deposited onto injection molded Si_3N_4 vane. This work was described in an interim report (AFML TR-79-4219, January 1980) and is briefly reviewed herein. The second effort went forward with a chamber modified as a result of the experience obtained in the first program. The material system used in the second series of the experiments was CNTD SiC, (CNTD SiC is a proprietary fine grained, strong SiC produced by a technique called Controlled Nucleation Thermochemical Deposition, U.S. patent number 4,239,819) deposited into a sintered SiC turbine blade.

Emphasis in this report is placed on the second program. Revisions to the reactor vessel are described as well as efforts to demonstrate turbulent flow. Deposition experiments and results obtained using the revised chamber will be given along with characterization of the material deposited.

Unclassified

FOREWORD

The work described in this report was performed under
Contract No. F33615-78-C-5161. Mr. K.S. Mazdiyasni of
the Air Force Materials Laboratory, Wright-Patterson AFB,
was the project monitor.

The authors would like to acknowledge helpful discussions
with Mr. Mazdiyasni and with Dr. Coles of the California
Institute of Technology. Messrs. Raja Takieddine and
Sebastian Cerna led the CVD techician group performing
the chamber fabrication and deposition experiments. In
addition Mr. Takieddine aided greatly in the writing of
this report. Thanks are due to Dr. D. Clingman, Detroit
Diesel-Allison, for providing sintered alpha SiC turbine
blades (manufactured by Carborundum Co.) for final demon-
stration runs in the new chamber.

Accession For	
NTIS GRA&I	✔
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

DTIC
COPY
INSPECTED
2

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

The program to be emphasized in this report encompassed eighteen months. This is in addition to the twelve month program reported on in AFML-TR-79-4219.[1]* As a result of the first year's effort a chamber was built in which Si_3N_4 was chemically vapor deposited on both graphite and then reaction bonded Si_3N_4 (RBSN) shapes. The principle employed was to raise the velocity of the reactant gas stream as high as possible in an attempt to reach the turbulent flow regime. Partial success was achieved in that a RBSN turbine vane was coated on all surfaces with chemically vapor deposited (CVD) Si_3N_4; however, the deposit did not have uniform thickness.

Encouraged by these results the follow-on effort was begun to further improve the performance of the chamber. A critique of our concept and chamber design was accomplished after the start of the follow-on program. This resulted in a shift of emphasis from a high velocity gas stream to imping-ing opposed reactive gas jets. During this period SiC was substituted for Si_3N_4 as the deposited material.

Deposition of CNTD SiC was emphasized. CNTD, Controlled Nucleation Thermochemical Deposition, is a proprietary process to San Fernando Labs (U.S. Patent No. 4,239,819) resulting in a very fine grained, strong deposited material.

---

*Superscript numbers in parentheses are references and are given at the end of the report.

SECTION I

INTRODUCTION

The initial effort under contract F-3361578-C-5161
with Chemetal Corp. began on 1 July 1978 and ended on
1 June 1979. The approach and accomplishments of the
aforementioned effort were described in a summary technical
report AFML-TR-79-4219 was printed in February 1980.

The results obtained warranted additional effort which
began on 1 January 1980 and ended on 1 June 1981. On
1 April 1980 Chemetal Corp. became a wholly owned subsidiary
of Dart Industries and changed its name to San Fernando
Laboratories (referred to as SFL, below).

This report describes only the work and accomplishments
made during the latter part of the program, (1 January 1980
to 1 June 1981). The reader is referred to the interim
report for a detailed discussion of the first year's efforts.

The problem addressed in this study is to coat a complex
substrate with a coating uniform in thickness consisting
of Si_3N_4 or SiC and to evaluate the coatings properties
as a structural ceramic materials. It was believed that
this procedure would upgrade the properties of a less
dense but easy to fabricate shape such as an injection molded
Si_3N_4 or SiC turbine blade or vane. Solving the problem
of putting a uniform structural ceramic coating on an
inexpensive easy to fabricate component is of interest to
the Department of Defense, specifically in improving the
performance and efficiency of limited life turbine engines.
An ability to increase the operating temperature of the
turbine section would help the development of such an
improved engine. However, efforts to increase the operating
temperature have been only marginal at best because of
a lack of materials suitable for the task. Although many
ceramic materials seem to possess some desirable high temperature

1

properties, no ceramic has yet shown that it has an appropriate combination of material properties and fabrication economy necessary to serve as a high temperatire turbine component.

CVD methods have demonstrated the ability to deposit ceramic materials with very desirable material properties; materials which, when deposited as a coating, might improve the performance of a turbine component made principally of some other material. CNTD materials, developed by SFL, with their extraordinary microstructure hold promise of even greater potential improvements over ordinary CVD materials.

This potential of CVD methods has been hampered, however, by an inability to form deposits uniformly on any but the simplest shapes such as bend bars. On a shape as complex as a turbine vane or blade a CVD coating would deposit very non-uniformly. The machining which would then be required would both compromise desirable material properties and at the same time render the process very much more expensive.

On any but the simplest and most symmetric of shapes, the CVD process has a serious handicap. The normal, laminar flow of gases over the surface to be coated will produce aerodynamic boundary layers near the surface. The CVD reaction can sometimes occur on the surface with a rate high enough to drain reactant species from within the boundary layer. In such a situation the surface reaction rate will be governed by mass transport kinetics of reactants through the boundary layer. Because the flow of gases over a complex shaped object will produce a boundary layer which varies in thickness over the surface of the object, the rate limitation imposed by this boundary layer will produce a very nonuniform coating over the surface.

Conventional methods which might be employed to achieve uniformity would do so by replacing mass transport through the boundary layers as the rate limiting step in the system.

For instance, the surface temperature of the object to be coated, which can be maintained uniform by radiant heating, might be reduced until the rate of the surface reaction

2

became the overall rate limiting factor for the entire surface.

Another method might rely on a reduction of the system's total pressure. As the pressure drops, the mean free path of gas molecules increases and the concentration of active species also drops. Boundary later diffusion rates then increase and the rate limiting factor shifts to the rate with which the general system atmosphere can supply reactants to the CVD reaction on the depositing surface.

Although both of these methods might solve the nonuniform coating problem, they do so at great expense to the general deposition rate and thus carry an economic penalty.

To avoid paying such a penalty, we chose to try to eliminate or at least greatly reduce, the boundary layer it-self.

SECTION II
FIRST APPROACH

Our analysis of the basic technical problem had convinced us that uniform CVD coatings might be achieved if we could eliminate or, at least reduce, the stable laminar boundary layer. We attempted first to bring about the <u>demise</u> of the laminar boundary layer through the use of higher velocity gas flows. We reasoned that, if the gases within the chamber could be made to flow fast enough over the part to be plated, we might cause the flow to leave the laminar regime and become turbulent. A turbulent flow would then promote excellent mixing of gas near the part surface with the free gas within the chamber and, thereby, promote a more uniform coating.[2,3] Our rationale for this approach is presented in more detail in AFML-TR-79-4219.[4]

Previous experience with the benefits of high velocity gas streams was gained from some work which had been conducted to develop refractory metal coatings for gun barrels. Armed with this experience, we proceeded to design a reactor based on our assessment of the technical requirements, as follows. If the reactant gases could be accelerated into the turbulent flow regime (Reynolds number, $N_{Re} \geq 2000$) or at least the upper laminar velocity regime (say $N_{Re} \geq 1000$), the major influence of the boundary layer surrounding the substrate might be minimized or eliminated. (See Appendix A in the interim report). Although, for the most part this expectation is reasonable, the value for the Reynolds number which we cite to describe the appropriate flow condition is wide of the mark.

The Reynolds number is a dimensionless quantity which is useful for describing the flow of a fluid whenever frictional forces are important. It is defined as the ratio of inertial forces (momentum) to frictional forces (viscous shear). For any specific flow system (as, for instance, within a pipe) the value of the Reynolds number describes the state of fluid flow regardless of the identity

4

of the fluid. Higher values of Reynolds number indicate the increased relative influence of inertial forces over frictional forces. At some critical value of the Reynolds number, $N_{Re,crit}$, flow within the system will change from purely laminar to partially turbulent. For flow within a straight pipe $N_{Re,crit} \cong 2000 - 2300$. The important fact that we seem to have been unable to find in the handbook treatises on fluid dynamics and that was lacking in our naive understanding of the subject, was that the value of $N_{Re,crit}$ is highly dependent on the local geometry of the solid surfaces over which the fluid flows.

Thus, even though initial experiments during the first year were done in cylindrical reaction chambers with gas flow parallel to the chamber axis, we wanted to design a more efficient chamber.

Cyclonic flow inside of, and perpendicular to the axis of a cylinder would also present a much different situation than axial flow down a straight pipe, and the transition to turbulent flow would undoubtedly occur at some value of $N_{Re,crit}$ other than 2300. The result of these design efforts is well documented in AFML-TR-79-4219. In spite of our lack of theoretical justification, the success achieved in depositing CVD Si_3N_4 on a reaction bonded Si_3N_4 turbine vane was encouraging[5]. All surfaces of the complex shape were coated. The coating, although well bonded and of uniform hardness, was non-uniform in thickness.

The first year's efforts also failed to produce the sought after fine grained modification of CVD Si_3N_4 namely, CNTD Si_3N_4. Some modifications to the microstructure of CVD Si_3N_4 were observed in Chemetal (San Fernando Labs) in-house efforts during the period of the first year's work. However, nothing approaching the grain refinement of San Fernando Labs CM 500 (fine grained tungsten/carbon alloy)[6] or CM 4000 (fine grained SiC)[7] was observed.

SECTION III
SECOND APPROACH

As the second program efforts began, we attempted to correct what we perceived to be shortcomings in the first reactor design.[8] It became apparent that our scant understanding of the aerodynamics of the problem was a hinderance. In addition, the very complex chemistry of Si_3N_4, itself, and lack of progress in determining parameters for CNTD Si_3N_4 deposition were frustrating, negative factors. After formal review of these topics in early 1980, it was decided to discontinue Si_3N_4 work in favor of SiC. The deposition parameters for CNTD SiC[7] were much better understood, in large measure due to AFOSR supported programs, [9,10] as well as internal (San Fernando Labs) development efforts.

To gain a better understanding of the fluid dynamics of our system, a consultant was retained for extensive discussions on the problem of creating turbulent gas flow conditions in the vicinity of a workpiece.[11]

The results of discussions with the consultant are as follows:

Our expectation of needing a Reynolds number, N_{Re}, of only $\cong 2300$ was excessively optimistic. It was pointed out that $N_{Re} \cong 10^6$ might be required to create local turbulent flow over a body having the dimensions and complexity of a small turbine blade. In order to achieve $N_{Re} \geq 10^6$, gas velocities would be required which were much higher than those achieved in any of our subscale testing. Fortunately, an alternative was available. The principle of opposing jets[12] presents an efficient method of generating turbulence at more manageable gas velocities.

To apply this concept, we built a transparent, plexiglass chamber in which cold gases (e.g. nitrogen) and later, water, could be used to model the fluid flow achieved with various nozzle designs and specimen placement schemes.

Reflective metallic particles (powdered aluminum) and small
glass beads were used to observe the various laminar
and turbulent flow spaces which developed during the experi-
ments. Lower velocities were required with water to produce
observable effects. Projections of behavior made in the
water chamber were then verified in a CVD experiment
incorporating graphite fibers and actual SiC deposition
in the altered centrifugal/opposed jet chamber. Both
types of experiments will be described more fully in the next
section on reactor chamber design and experiments.

SECTION IV

CHAMBER DESIGN AND
DEPOSITION EXPERIMENTS

As a result of consultation and our own experiments in the gas and water chambers, we undertook major revisions to the chamber which existed at the close of the first year's work. The purpose of this section is to describe the various flow pattern experiments which were done, the results obtained and the changes in chamber design which we made. The experiments were performed, and will be described in the following order. First, flowing water containing aluminum particles or small glass beads was used to investigate flow patterns from opposing jets set at various angles to each other. Observations were made of the various flow patterns and an optimum angle chosen. Next, CVD experiments were carried out to develop deposition parameters for CNTD SiC while exploring the effects of opposing jets on gaseous flow fields. These experiments were done with graphite flexure bar substrates, a complex graphite cross (described more fully below), and sintered SiC turbine blades.*

Water Experiments

We wanted to empirically verify the effectiveness of the opposing jets approach in generating turbulent flow. Tests were performed in an annular shaped reactor (see Figures 1 and 2) made of plexiglass and having a cylindrical center piece, PVC nozzles, and water as the working fluid.

Two sets of nozzles were used, one for high pressure (80 psi) water flow with the water jet streams opposing each other at an angle, and another set having a low water pressure (20 psi) which carried aluminum particles or small glass spheres into the chamber.

The turbulent "eddy" flow was monitored by directing a strong light source through the chamber as in Figure 2.

---

*Sintered α-SiC blades fabricated by Carborundum Co. were obtained through the courtesy of Dr. David Clinaman, Detroit Diesel Allison Div., General Motors.

1. CENTER PIECE
2. RADIAL JET NOZZLE
3. CHAMBER TOP PLATE
4. WATER INLET
5. WATER INLET
6. ORIFICE
7. CHAMBER WALL
8. OPPOSING JET NOZZLE
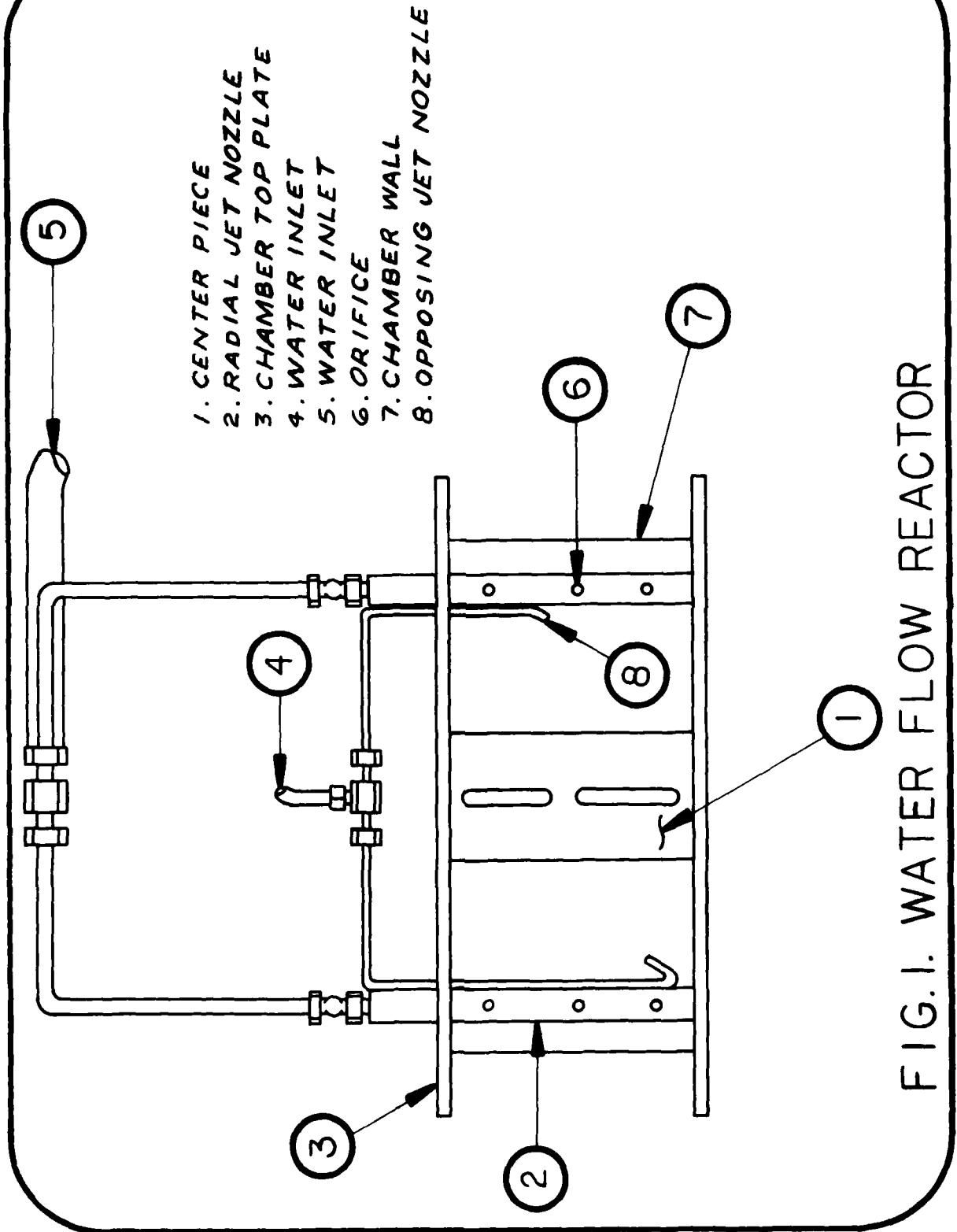
FIG.I. WATER FLOW REACTOR

9
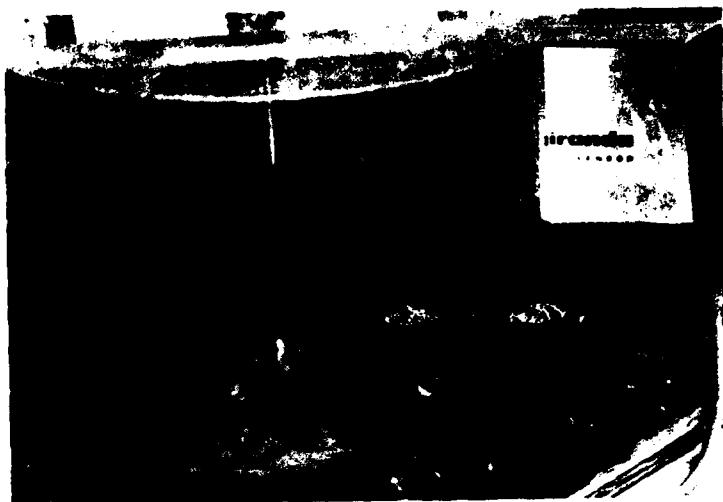
FIGURE 2   Turbulent Flow inside water reactor

Two parameters were varied during the experiments:
The angle between the high pressure opposed jets and the
orifice sizes of the nozzles and the cylindrical center
piece. The angle between the high pressure jets was found
to influence the intensity of the turbulent flow, and the
orifice size on the exhaust centerpiece determined the
velocity of the discharge and the circulation pattern
inside the chamber.

It was found that an opposed jets angle of 160°-180°
gave a strong turbulent flow pattern with low water cir-
culation while 90°-130° resulted in weak turbulence and
much circulation around the chamber. An angle of 130°-160°
gave a fairly high turbulence with medium circulation
velocity.

Final Reactor Design

Based on the results of the water flow experiments
and problems encountered during the preliminary deposition
runs, many design changes had to be made on the initial
reactor to achieve the best performance.

The initial nozzle orientation and the sizing of
the discharge orifices and exhaust center piece were ob-
tained from the water experiments, but due to the tendency
of the active gas to deposit on the inside of the alumina
injectors which caused them to crack, these injectors
were relocated away from the reactor wall towards the center
where they are exposed to a lower temperature. Also
graphite sleeves were added over the injectors to prevent
any SiC deposition which tends to weaken the alumina.

The orifice size of the active gas nozzles was
increased from 50 to 90 mils diameter. Graphite foil and
felt ($\frac{1}{2}$" thick) was used around the outside walls of the
reactor to prevent excessive heat loss to the surroundings.
Figures 3(A) and (B) illustrate the final design of the
reactor while Figure 4 shows the design orientation of the
discharge nozzle.

1. TABLE TOP
2. ALUMINA NOZZLES
3. GRAPHITE CENTER PIECE
4. THERMOCOUPLE (ALUMINA SHEATH)
5. QUARTZ EXHAUST TUBE
6. GRAPHITE NOZZLE COVERS
7. TYPE "K" THERMOCOUPLE
8. RUBBER BOTTOM
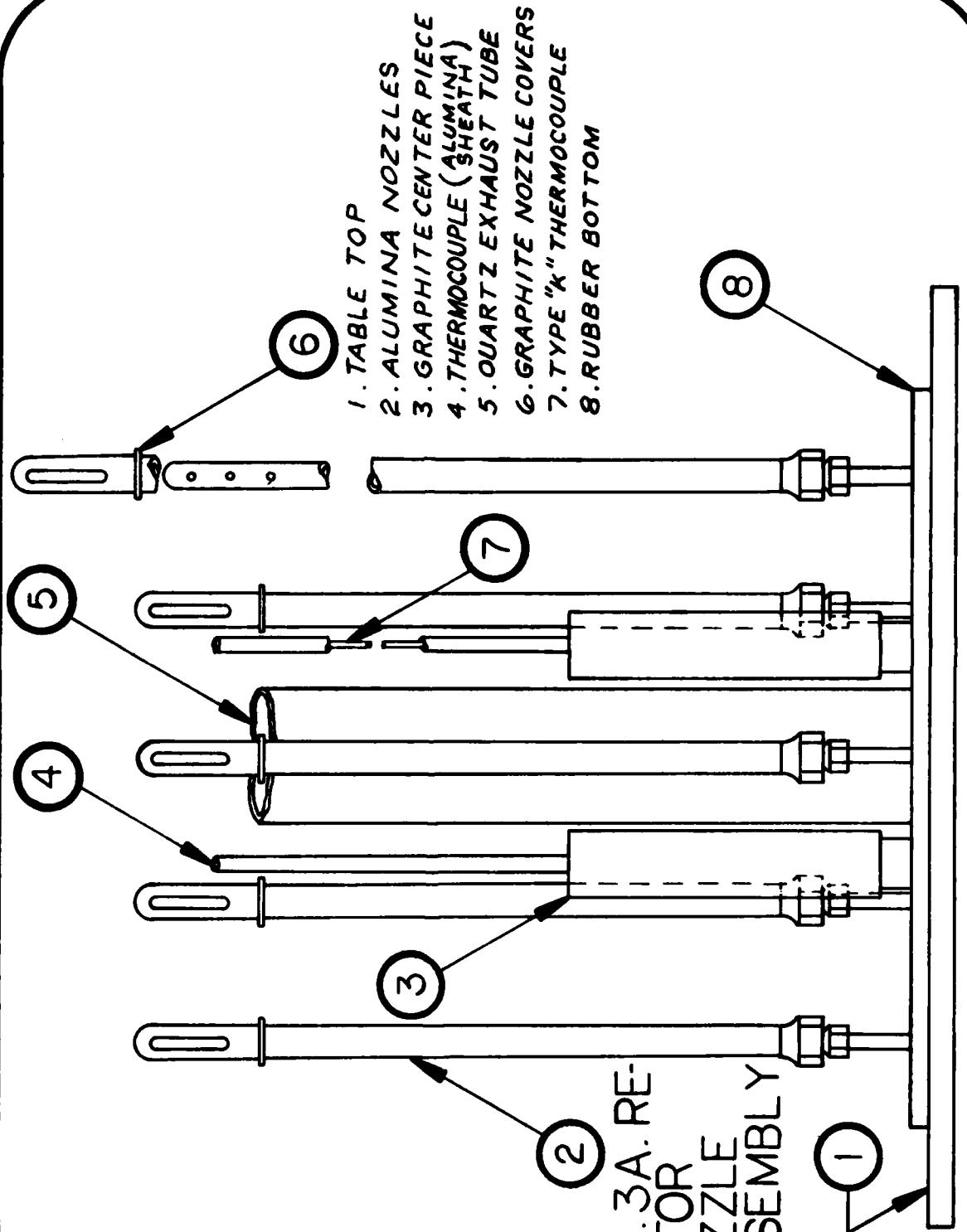
FIG. 3A. RE-ACTOR NOZZLE ASSEMBLY

1. = REACTOR FURNACE
TOP COVER
2. = REACTOR FURNACE
WALL
3. = GRAPHITE FELT
4. = FURNACE BOTTOM
PLATE
5. = FURNACE EXHAUST
6. = GRAPHITE FURN-
ACE SUPPORT
7. = GRAPHITE STRING

FIG. 3B. REACTOR ASSEMBLY

NITROGEN & HYDROGEN
INJECTOR

ACTIVE GAS
INJECTOR

LOCATION OF
SUBSTRATE FOR
DEPOSITION
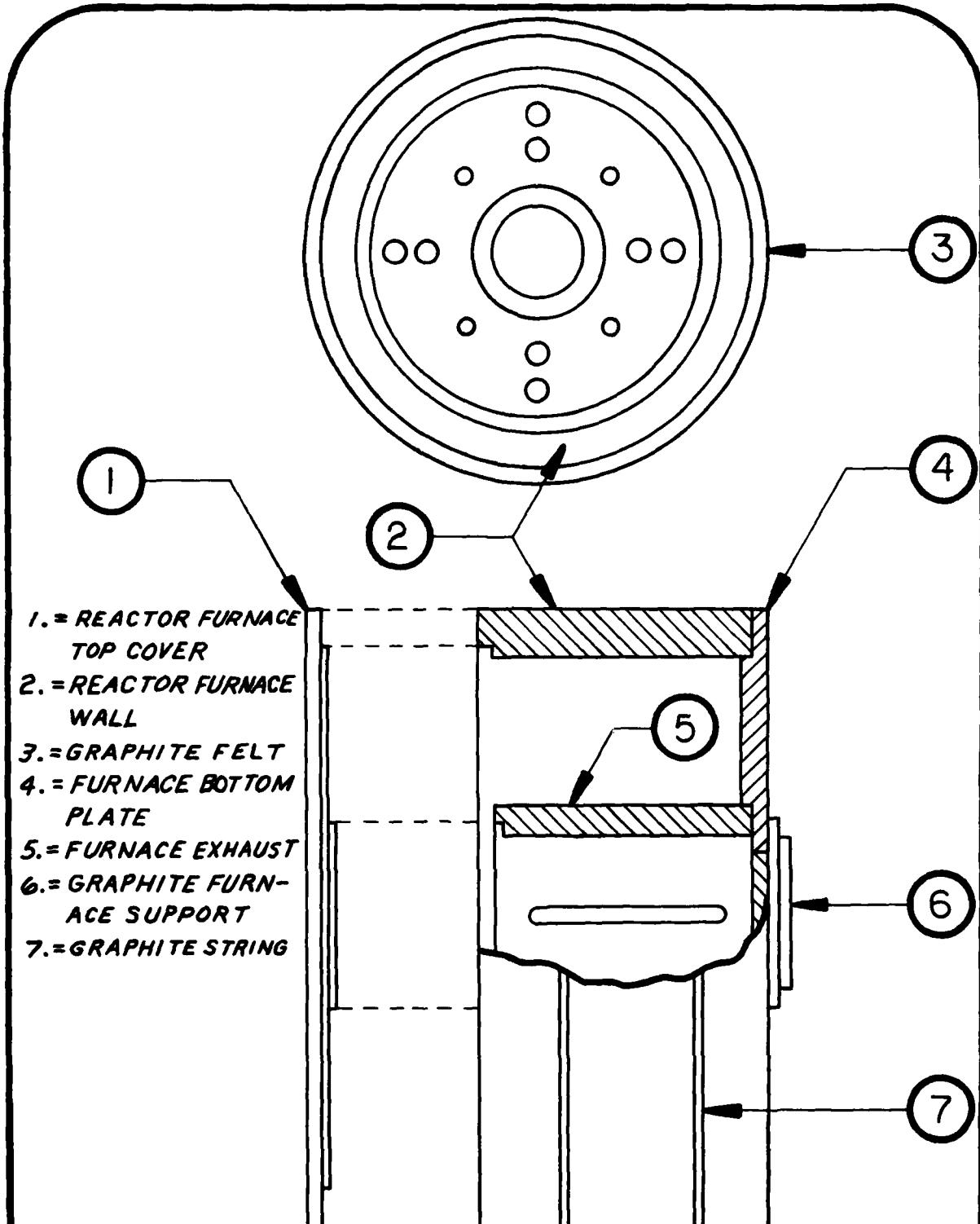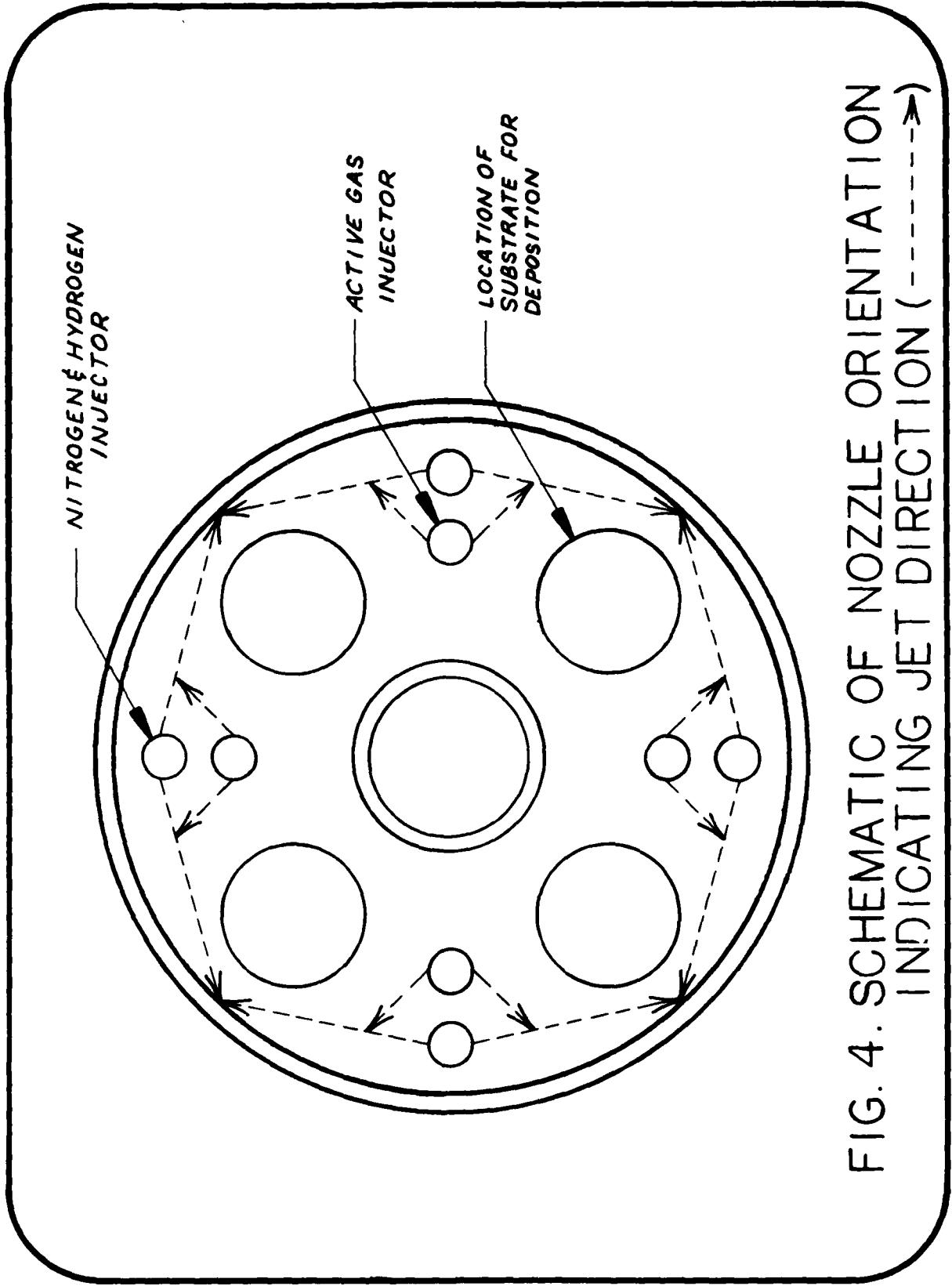
FIG. 4. SCHEMATIC OF NOZZLE ORIENTATION
INDICATING JET DIRECTION (- - - ->)

14

Deposition Experiments

The primary objective of the experimental deposition runs was to minimize the variation in the coating thickness of the material deposited. Three kinds of experiments were performed:

A.   Preliminary Deposition Experiments

In order to develop an acceptable SiC material for deposition on complex shapes, graphite flexure bar specimens were used as substrates due to their shape advantage which permits easier evaluation of the physical and mechanical properties of the material.

To obtain the run conditions for a SiC which would provide initial characterization data, three parameters were varied: Temperature, Total pressure, Hydrogen to Methyl-trichlorosilane (MTS) ratio. Table I shows those conditions under which an acceptable material was deposited.

B.   Graphite Filament Flow Modeling Experiments

Eight inch long (.006" O.D.) graphite filaments were glued to graphite rods and placed inside the furnace in a circular orientation around an imaginary part, with one rod standing at the center representing the part itself, Figure 5A.

After two hours of deposition, the filaments were coated with SiC and frozen. Being light in weight, the filaments were directed by the turbulent gas flow before being frozen. This procedure gave a clear idea of the gas flow pattern inside the furnace and surrounding the substrate.

A high concentration of frozen filaments was re-corded on the rods close to the furnace wall, the area at which the two opposing jets met. This high concentration section measured 2½ inches at its widest portion and narrowed toward the center of the circle (see Figure 5B) and C). The lowest concentration of fibers was located in the sector close to the exhaust center piece.

C.   Deposition Experiments using "T" Shaped and Turbine Blade Specimens

The main purpose of these experiments was to derive

15
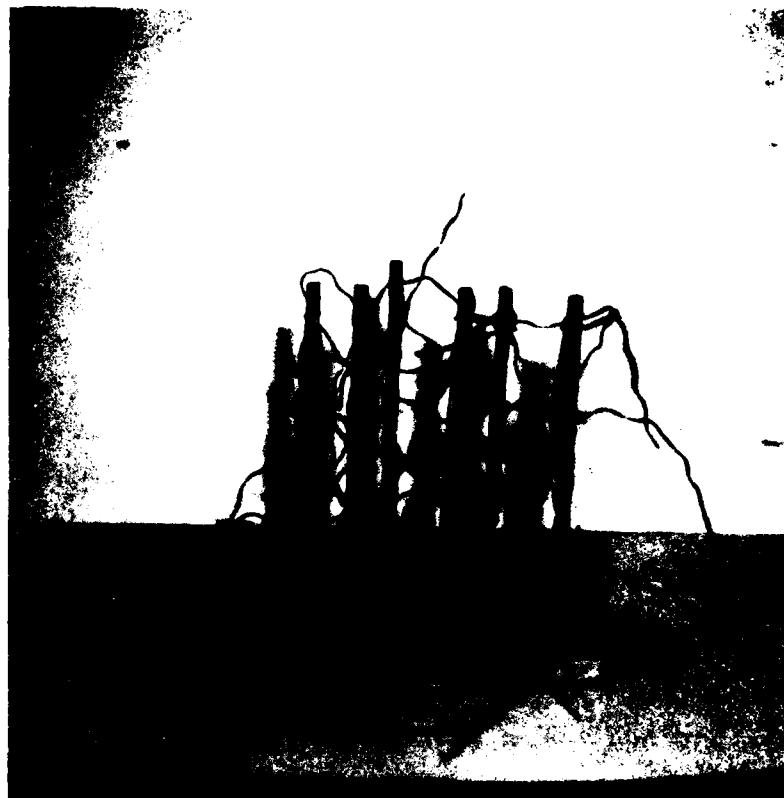
FIGURE 5A   Graphite Filaments before SiC Deposition

16
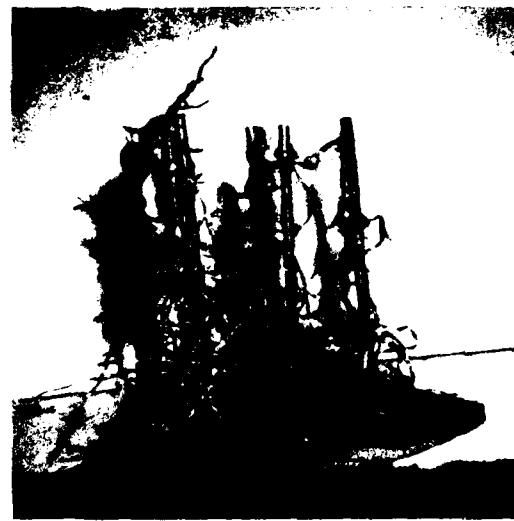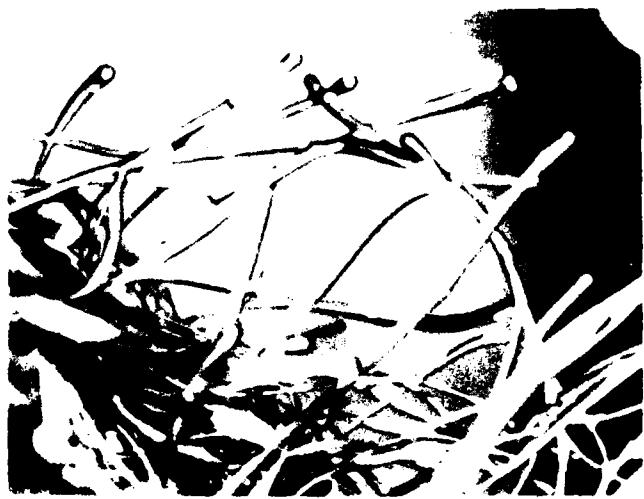
FIGURE 5B   SiC Coated graphite filaments

17
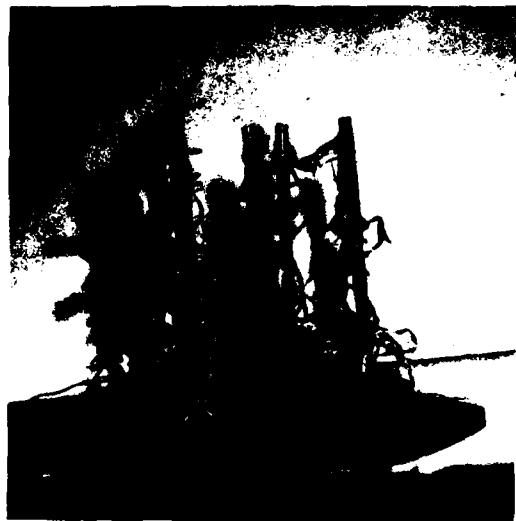
FIGURE 5C   Graphite Filaments after SiC deposition

18
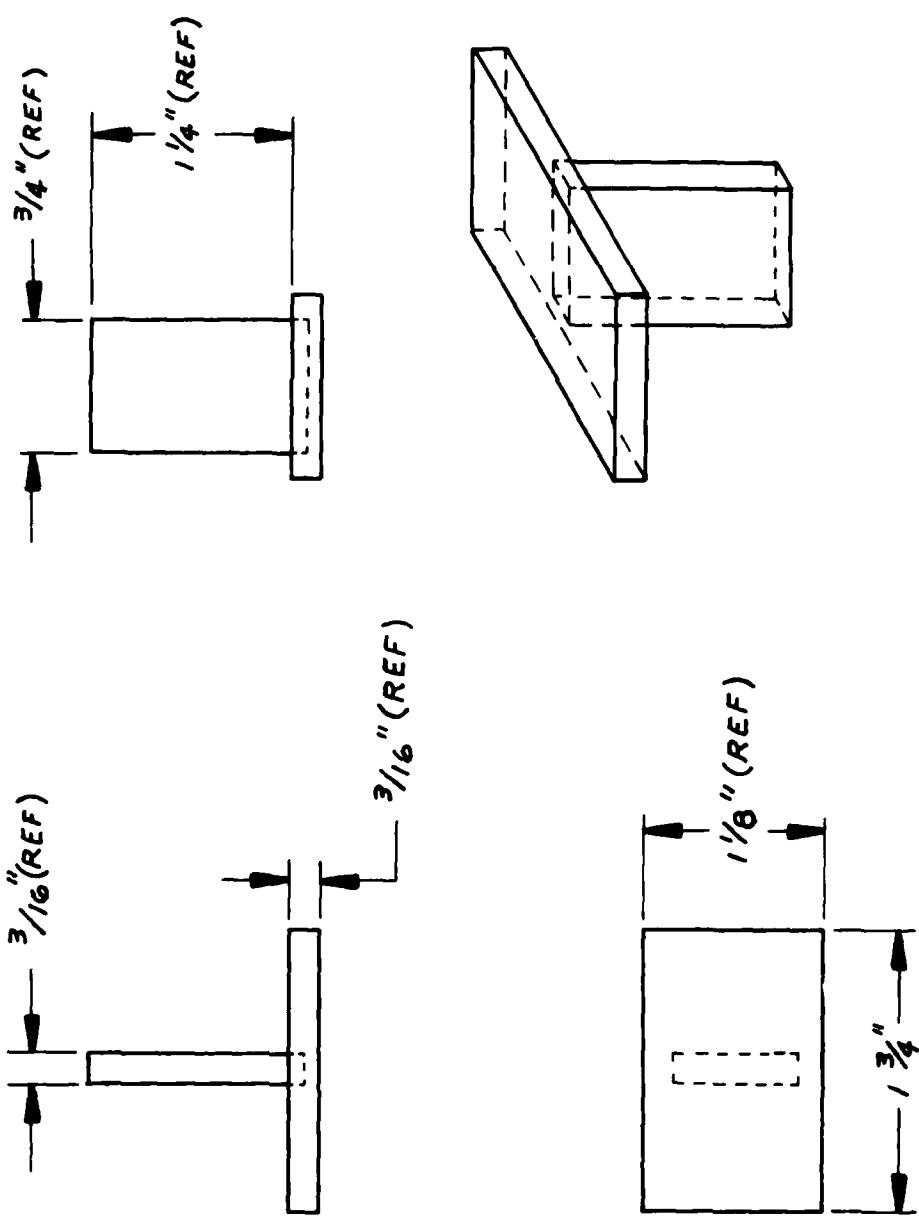
FIG. 6A. COMPLEX "T" TEST SPECIMEN
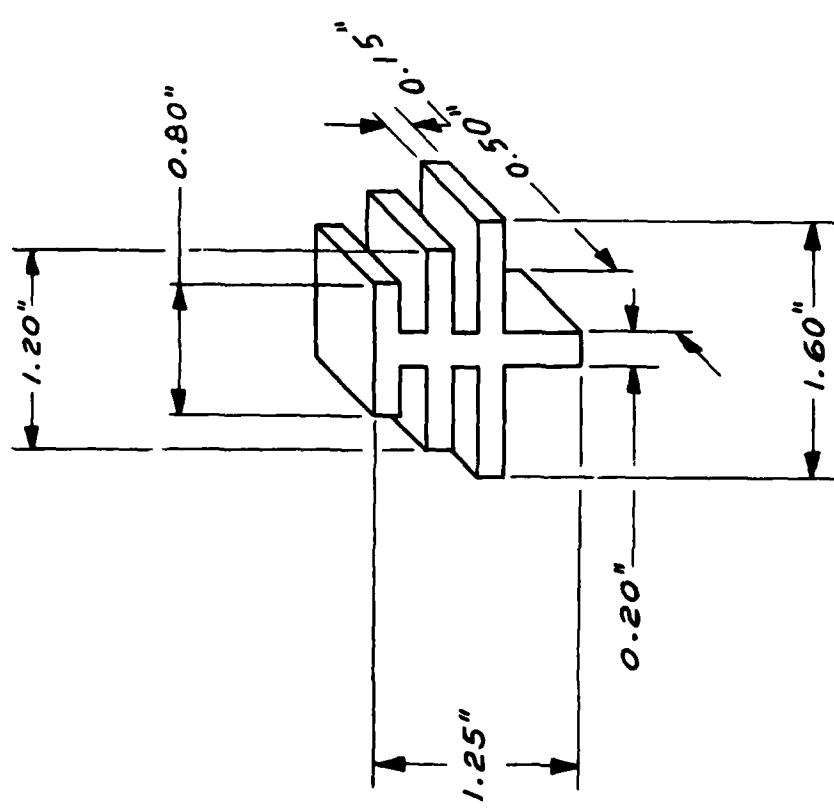
FIG. 6B. MULTI "T" COMPLEX SPECIMEN

FIGURE 6-C   Sintered SiC Turbine Blade to be deposited.

TABLE 1   RUN PARAMETERS FOR TURBULENT CHAMBER
SiC DEPOSITION INITIAL MATERIAL

PART TEMPERATURE (°C)	TOTAL PRESSURE (TORR)	HYRODGEN FLOW CC/MIN	MTS FLOW CC/MIN	INSIDE FURNACE NITROGEN FLOW CC/MIN	OUTSIDE FURNACE NITROGEN FLOW (CC/MIN)	MTS CARRIER NITROGEN FLOW CC/MIN
1140	200	20000	1200	16000	3000	1100

22

TABLE 2   OPTIMUM RUN CONDITIONS FOR DEPOSITING (fine grain)

SiC COATINGS ON COMPLEX SHAPE

PART TEMPERATURE (°C)	TOTAL PRESSURE (TORR)	HYDROGEN FLOW CC/MIN	MTS FLOW CC/MIN.	INSIDE FURNACE NITROGEN FLOW CC/MIN.	OUTSIDE FURNACE NITROGEN FLOW CC/MIN	MTS CARRIER NITROGEN FLOW CC/MIN
1108	250	22000	1200	14000	10000	1100

23

the turbulent flow parameters for deposition of SiC onto complex shapes. These shapes are represented as follows: A graphite "T" shape (Figure 6A), a graphite multi "T" shape (Figure 6B), and a sintered alpha silicon carbide turbine blade (Figure 6C) obtained from D. Clingman, Detroit Diesel-Allison and fabricated by the Carborundum Company.

To start with, the same run conditions which proved to be the best for deposition on flexure bars (Table I) were used. The deposited material was very uneven on both of the "T" shapes, especially around the inside sharp corners. Figure 7 shows the initial thickness uniformity results on the simple "T" shape. By systematic adjustment of three run parameters: temperature, total pressure, and nitrogen flow rate, the uniformity was substantially improved. Increasing the pressure yielded better uniformity in the coating thickness. This we think is due to the increase in the turbulence produced. A temperature range of 1100°C - 1115°C proved to be essential for uniform coating thickness while the most uniform coating was obtained at a temperature of 1108°C. Higher temperatures yielded a very rough surface, and lower temperatures resulted in an "edge effect" wherein the coating was thicker at the edge and decreased substantially away from the edge.

Increasing the nitrogen mass flow enhanced uniformity until the cooling effect of the gas flow became dominant and started to cause the edge effect mentioned above.

Table II shows the optimum run conditions used for obtaining the best and most uniform coatings on complex shapes. Figure 8 shows the variation in coating thickness on a "T" shape after optimization of deposition parameters. Run conditions shown in Table 2 were used to deposit SiC on reaction bonded Si_3N_4 (RBSN) shapes, sintered SiC turbine blades, and a more complex multi "T" shape. These results are discussed in detail in the next section.
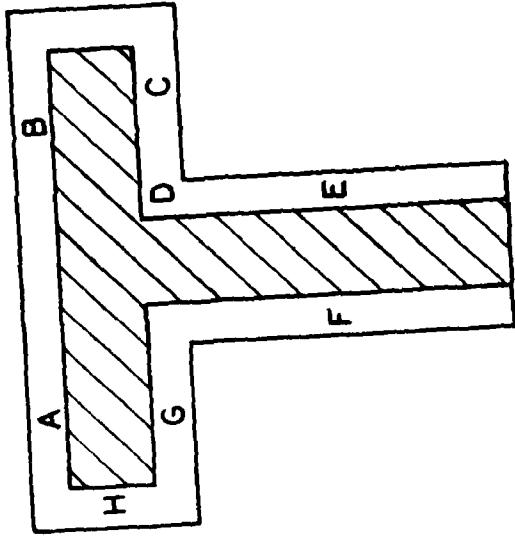
COATING THICKNESS (μM)
A = 78.74
B = 124.46
C = 33.02
D = 5.08
E = 40.64
F = 48.26
G = 45.72
H = 36.83

FIG. 7. CROSS SECTION VIEW OF "T" SiC
THICKNESS (INITIAL RESULTS)

25

COATING THICKNESS (μm)

A = 71.12
B = 63.5
C = 58.42
D = 68.58
E = 48.26
F = 68.58
G = 66.04
H = 46.23
I = 63.5
J = 62.23
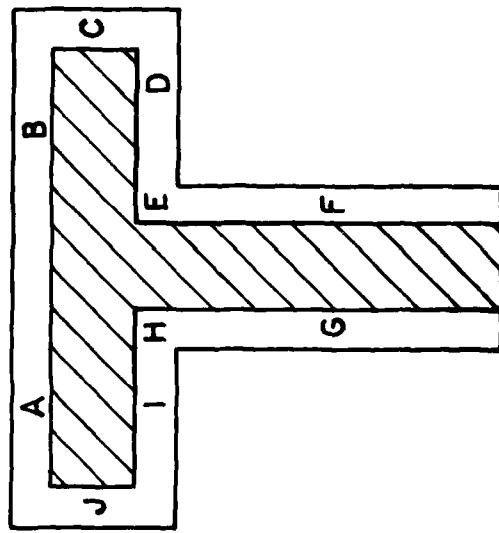
FIG. 8. OPTIMUM SiC DEPOSIT UNIFORMITY
ON "T" SHAPE

SECTION V
MATERIAL CHARACTERIZATION

A. Uniformity

Extensive evaluation of the SiC coating thickness on complex shape surfaces of a turbine blade (Figure 9) as well as the simple "T" shape (refer to Figure 8), and multi "T" shape (Figure 10), showed a major improvement in minimizing the variation of the coating thickness. A direct relationship was observed between the degree of turbulence which is a function of total pressure and gas flow rate, and the percent variation in the coating thickness. The coating thickness variation reached a maximum value on a "T" shape specimen deposited in an axial flow, cylindrical laminar flow furnace.

B. Sic Deposited in the Turbulent Flow Reactor

Characterization of the material deposited on complex specimens included microstructural analysis, x-ray diffraction analysis and hardness evaluation. The results indicated a high silicon content (Table 3) in SiC fine grain material (Figure 10) deposited on a complex "T" shape with low hardness values. While material deposited at a higher temperature (1135°C compared to 1110°C) and lower pressure (170 Torr compared to 250 Torr) exhibited lower silicon content with higher hardness and TRS values (Table 4). Metallographic examination of the cross section of this material showed a mixed structure containing columnar growth and fine grained material with a rough outer surface as shown in Figure 12.

C. CNTD SiC in a Straight-Through Flower Pot Furnace

Acting on a request from the project monitor, thirty flexure test specimens of CNTD SiC on polished graphite (grade SIC 6, Graphite Systems) substrates were furnished to IIT Research Institute for test and evaluation. Flexure strengths were obtained at various temperatures shown in Table 5 and 6. These showed a wide range of values when tested at a given temperature. We believe this variation

27

MAT'L: SiC
SUBSTRATE: Si₃ N₄ TURBINE BLADE
PART NO.: 9A-4491-29-4
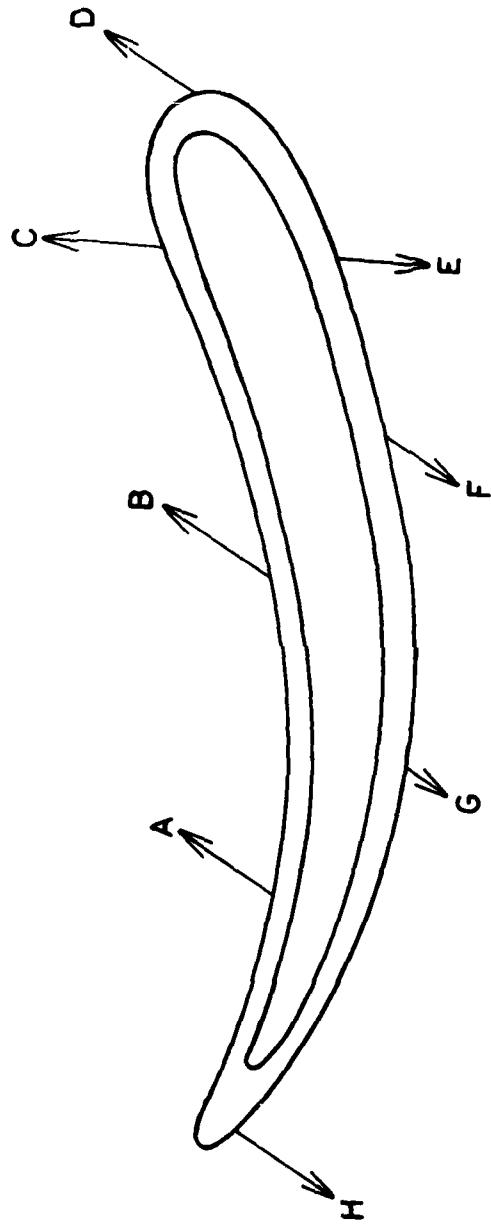
LOCATION	THICKNESS(µM)	HARDNESS/HV200
A	55.88	1220
B	92.00	1396
C	86.36	1314
D	73.66	1626
E	66.04	2000
F	76.20	1224
G	78.74	1355
H	73.66	1120

FIG. 9. COATING THICKNESS ON RBSN
Si_3N_4 TURBINE BLADE
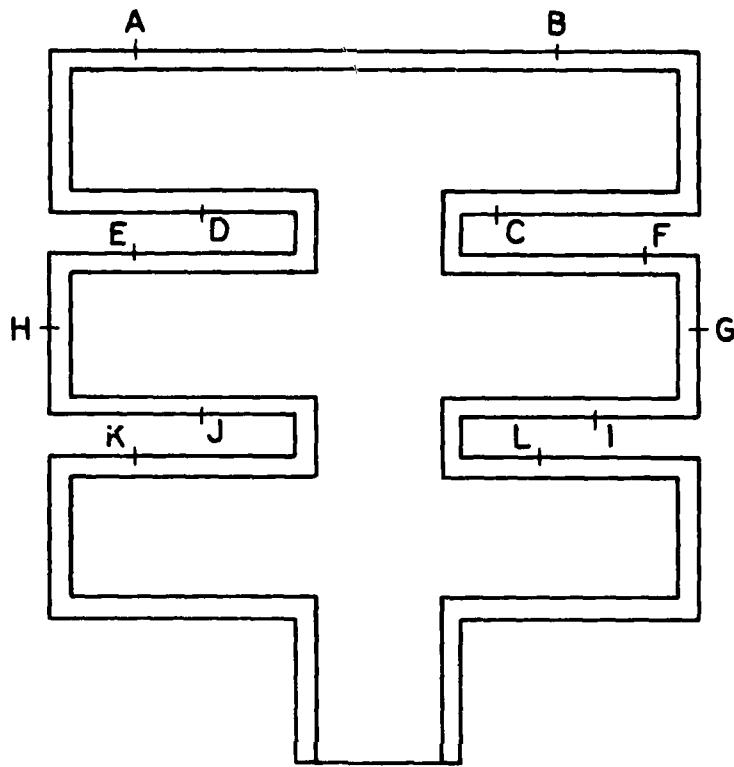
COATING THICKNESS (μM)

A = 83.82		H = 76.2
B = 81.28		I = 63.51
C = 48.26		J = 49.53
D = 63.51		H = 76.20
E = 65.30		K = 43.20
F = 60.96		L = 53.34
G = 78.74		

FIG. 10. COATING THICKNESS ON MULTI "T" COMPEX SHAPE

TABLE 3   XRD and other data for specimen shown in Figure 10

Material: SiC/SiC$_6$ Graphite   Run #9A-4491-39-153

Position of Peak 2θ, deg.	dhkl From Tables, Å	β-SiC d$_{hkl}$	ASTM card (1-119) hkl	2θ, deg.	Si d$_{hkl}$	Si ASTM Card No. 5-0565 hkl	Si ASTM Card No. 5-0565 2θ, deg.
24.5	3.6302						
28.65	3.1291				3.138	111	28.4
35.6	2.5196	2.51	111	35.75			
47.4	1.9163				1.92	220	47.3
56.2	1.6353				1.638	311	56.1
60.2	1.5359	1.54	220	60			
69.2	1.3564				1.357	400	69.2
71.8	1.3136	1.31	311	72			
76.6	1.2428				1.246	331	76.4
88.2	1.1068				1.1083	422	88.1

30

TABLE 4   XRD and other data for specimen shown in Figure 11

Material: SiC/SiC₆   Graphite   Run 9A-4491-28-153

Position of Peak 2θ, deg.	d_hkl From Tables Å	I/I_max	β-SiC ASTM Card No. 1-1119			Si ASTM Card No. 5-0565		
			d_{hkl}	2θ (deg.)	hkl	d_{hkl}	2θ (deg.)	hkl
35.6	2.5196	100	2.51	35.75	111			
47.4	1.9163	30				1.920	47.3	220
54.3	1.6879	2						
56.15	1.6366	20				1.638	56.1	311
60.0	1.5405	9	1.54	60	220			
69.2	1.3564	2				1.357	69.2	400
71.7	1.3152	5	1.31	72.0	311			
75.4	1.2596	22	1.26	75.4	222			
76.3	1.2470	5				1.246	76.4	331

31

TABLE 5[13]   4-POINT BEND STRENGTH OF CHEMETAL (SFL)

CNTD SiC

BATCHES 3 and 4

	25°C	
Sample		Strength psi
Batch 3 on Polished SIC 6 Graphite Substrate		
CS3F1		108,630
CS3F2		111,990
Batch 4 on Polished SIC 6 Graphite Substrate		
CS4F1		84,780
CS4F2		61,560

	1200°C		25°C after 15 min/ 1200°C Pre-Exposure	
Sample	Strength psi		Sample	Strength psi
Batch 3, on Polished SiC 6 Graphite Substrate				
CS3F3	50,020		CS3F4	90,240
CS3F6	55,280		CS3F5	94,940
Batch 4, on Polished SIC 6 Graphite Substrate				
CS4F3	156,600		CS4F6	160,020
CS4F4	111,840		CS4F7	185,390
CS4F5	111,560			

	1500°C	
Sample		Strength psi
Batch 3 on Polished SIC 6 Graphite Substrate		
CS3F8		56,700
CS3F9		50,930
CS3F10		63,800
Batch 4 on Polished SIC 6 Graphite Substrate		
CS4F8		54,320
CS4F9		38,860
CS4F10		41,770

TABLE 6[13]

4-POINT BEND STRENGTH OF CHEMETAL (SFL) CNTD SiC,
BATCHES 1 and 2

| | 25°C | | 1200°C | |
| | Strength | | | Strength |
Sample	psi		Sample	psi
		Batch 1,		
	On UT-22 Graphite Substrate			
CS1F1	27,890		CS1F6	54,480
CS1F2	45,360		CS1F7	54,760
CS1F3	27,640		CS1F8	53,830
CS1F4	27,870		CS1F9	72,010
CS1F5	60,450		CS1F10	62,490
		Batch 2,		
	On SIC 6 Graphite Substrate			
CS2F1	119,180		CS2F3	28,680
CS2F2	85,320		CS2F5	150,490

is caused by one or more of the following: Material variation due to the variation in process parameters, the graphite substrate probably possessed defective geometry caused by hand grinding and polishing. It was indicated that the 50 ksi strength at 1500°C is the result of high purity of the chemically vapor deposited coating[13].

In order to compare the uniformity of deposits in a "standard", straight through furnace with the turbulent reactor, a "T" specimen was run in the standard furnace. The resulting deposit was less uniform and some corners were not as well coated as were portions more exposed to the gas stream. This is illustrated by comparing Figure 11 with Figure 8 or 10.

COATING THICKNESS (μM)

A = 99.06
B = 104.14
C = 30.48
D = NONE
E = 53.34
F = 35.56
G = 20.32
H = 73.66
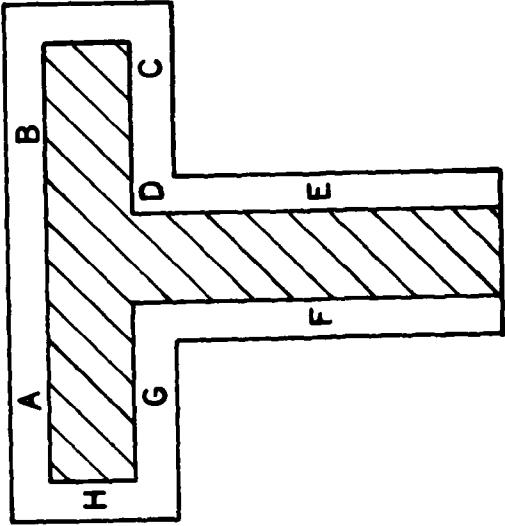
(FIG. 11.) COATING THICKNESS OF SiC DEPOSIT ON A "T" IN STRAIGHT THROUGH FURNACE

SECTION VI
DISCUSSION AND CONCLUSIONS

The use of opposing jet flow to create a turbulent medium around the part to be coated proved to be a major step forward in controlling the effect of the boundary layer, hence minimizing the variations in the SiC deposited layer thickness. Eddy motion was observed in the graphite filament experiment. The results achieved are encouraging because the present reactor had no provision for preheating the gases. In other words, the gases were introduced to the turbulent flow furnace at room temperature while in the conventional CNTD process (i.e. an axial flow, once through furnace) the gases were preheated to 400°C before being introduced to the furnace.

The coating thickness obtained on all parts examined by metallography showed a variation of 4 mils (102μ) to 1.5 mils (38μ) compared with a variation of 9 mils (229μ) to 0.75 mils (18.9μ), see for example Figure 18, Reference Number 1.

Two major problems were encountered in the turbulent flow reactor: The initial deposition runs showed a high silicon content in the deposited materials which caused a low hardness ($\sim$1100 HV_{500}) and TRS, 38 ksi (260 MPa), Table 3. This is an indication of a low gas temperature at the part. Control of gas temperature going into the furnace was not possible due to design limitations, however two methods were used to increase the gas temperature within the reactor. First, the overall temperature was increased from 1110°C to 1150°C. The result was a deposit having a rough and uneven surface and a duplex grain structure showing substantial columnar growth along with a banded structure characteristic of high strength, fine grained CNTD SiC (refer to Figure 13). Secondly, the hydrogen mass flow rate was increased from 11 liters/min to 20 liters/min, which caused the silicon content in the deposit to decrease

36
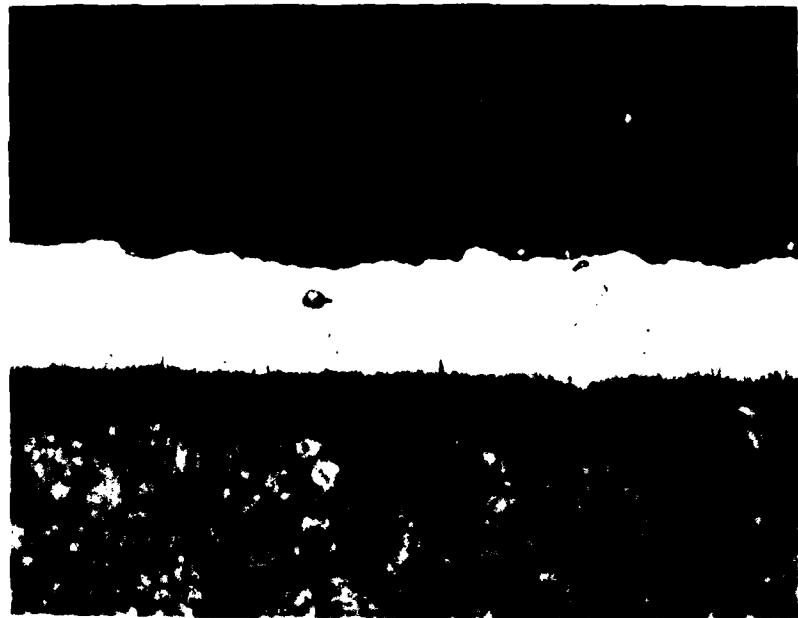
FIGURE 12   Cross Section of Material deposited at
1135°C and 170 TORR.
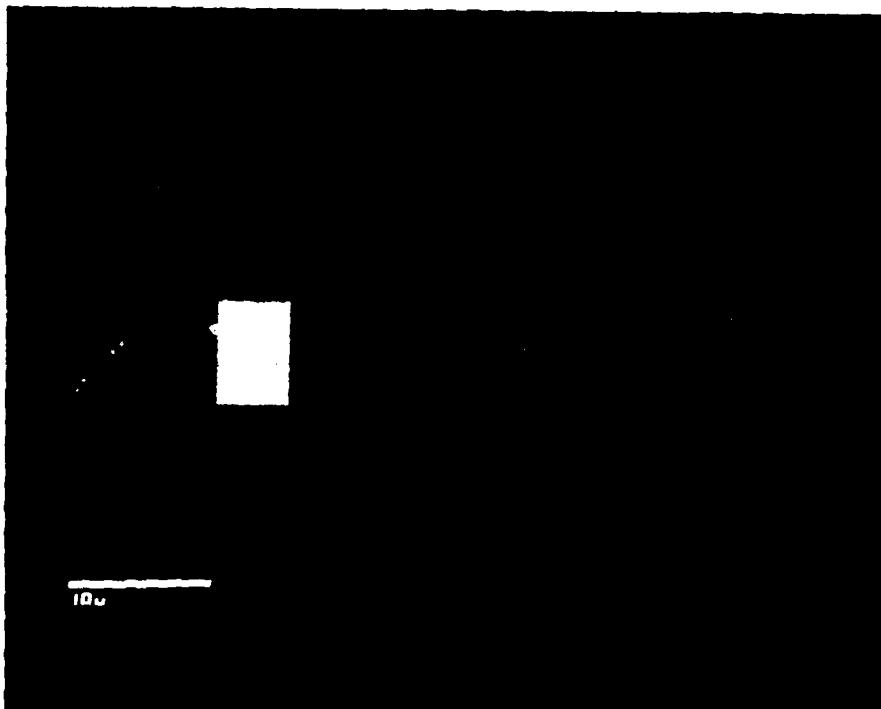
FIGURE 1: Cross Section of fine grain material
deposited at 1108°C and 250 TORR

38

along with a drop in the deposition rate from 4 mil/hr to 1.5 mil/hr. In addition, an increase in the deposition of SiC over the furnace walls was evident.

The conclusions reached in our efforts to develop complex shape coating techniques are as follows:

1. We have demonstrated the potential of a turbulent flow reactor to provide a more uniform CVD coating on complex shapes.

2. We have demonstrated the use of opposing jets to create a turbulent environment surrounding a complex shape, such as a turbine blade.

3. We have demonstrated a potential for scaling up the CNTD SiC process into larger reactors. This would be a significant advantage in a production situation.

REFERENCES

		PAGE
1.	R. Holzl, Investigation of CNTD Si_3N_4 on Complex Shapes, Interim Report, Contract F33615-78-C-5161, AFML-TR-79-4219.	vii
2.	W. Christian and S. Kezios, A.I. Ch. E. Journal, Vol. 5 (No. 1), March 1959, p. 61.	4
3.	W. Linton and T. Sherwood, Chemical Engineering Progress, Vol. 46 (No. 5), May 1950, p. 258.	4
4.	R. Holzl, Investigation of CNTD Si_3N_4 on Complex Shapes, Interim Report, Contract F33615-78-C-5161, AFML-TR-79-4219, P. 7.	4
5.	R. Holzl, ibid., pp. 32-54.	5
6.	CM 500 Patent No. 4,147,820.	5
7.	CM 4000 Patent No. 4,239,819.	5
8.	R. Holzl, Investigation of CNTD Si_3N_4 on Complex Shapes, Interim Report, Contract F33615-78-C-5161, AFML-TR-79-4219, pp. 55-59.	6
9.	R. Holzl, An Investigation of the CNTD Mechanism and Its Effect on Microstructural Properties, AFOSR-49620-77-C-0086- 1977.	6
10.	R.M. Panos, D.G. Bhat, An Investigation of the CNTD Mechanism and Its Effect on Microstructural Properties, AFOSR-49620-79-C-0041-1977.	6
11.	P. Witze and H. Dwyer, Proceedings of the Symposium on Turbulent Shear Flow, University Park, PA. (18-20 April 1977), p. 233.	6
12.	Prof. D. Coles, Dept. of Aeronautics and Astronautics, California Institute of Technology, Pasadena, CA, Private Communication.	6
13.	Larsen, D.C. and Adams, J.W., IITRI Semi-annual Report No. 9, AFML Contract No. F33615-79-C-5100, December 1980.	34